

EFFECT OF PRODUCTION CONDITIONS ON THE PROPERTIES AND MICROSTRUCTURE OF $\text{Ce}_{0.1}\text{Al}_{0.1}\text{Zr}_{0.8}\text{O}_2$ NANOPOWDER BASED COMPOSITE CERAMIC

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A comparative analysis is performed of the microstructural and mechanical particularities of composite ceramic materials obtained from $\text{Ce}_{0.1}\text{Al}_{0.1}\text{Zr}_{0.8}\text{O}_2$ nanopowder synthesized by three methods — in the presence of urea, in the presence of hexamethylenetetramine, and using an aqueous solution of ammonia as the main agent. It is established that $\text{Ce}_{0.1}\text{Al}_{0.1}\text{Zr}_{0.8}\text{O}_2$ powder synthesized in the presence of hexamethylenetetramine and the ceramic obtained from this powder have superior properties.

Key words: composite ceramic, zirconium dioxide, cerium dioxide, nanopowder, cold isostatic pressing.

Stabilized zirconium dioxide ZrO_2 is interesting as a ceramic material possessing useful optical, electric, thermal, strength and other properties [1–3]. The combination of high viscosity (comparable to that of steel), hardness, chemical inertness and low coefficient of friction makes this ceramic a promising, wear-resistant material, which is suitable for use in orthopedic dentistry. In addition, ZrO_2 based ceramic articles have good inherent properties such as colorfastness, color close to that of natural teeth (which meets aesthetic requirements), nonallergenicity, and no negative effects on oral cavity tissue.

The improvement of the mechanical properties of ceramic based on yttrium stabilized zirconium dioxide is due to hardening as a result of a structural phase transition from one crystal modification of ZrO_2 to another, which is accompanied by an increase of the local compressive stresses impeding crack propagation [4]. Today, it is yttrium-zirconium ceramic that is a natural, absolutely reliable material for restoration of the grinding teeth and makes it possible to fabricate structures with minimal wall thickness and area of connecting elements without loss of strength [5–7].

However, ceramic based on yttrium stabilized zirconium dioxide is characterized by an aging process associated with an undesirable phase transition of the cubic and tetragonal modifications of ZrO_2 into a monoclinic modification that is accompanied by a material volume increase (to 6 vol.%) and depends on many factors (chemical and phase composition,

grain size, morphology, presence of residual stresses and so on). Initially, the aging process increases the roughness of the polished working surface of implants (i.e., wear increases) and ultimately, when the content of the monoclinic phase becomes substantial, leads to complete decomposition. For this reason, the elimination or, at least, reduction of the effect of this process on the performance of implants is a topical problem [8, 9].

One possible solution could be replacing yttrium oxide with other stabilizing dopants, specifically, cerium oxide.

The objective of the present work is to study the effect of the method used to synthesize $\text{Ce}_{0.1}\text{Al}_{0.1}\text{Zr}_{0.8}\text{O}_2$ powder on the microstructure and mechanical properties of composite ceramic materials.

We note that, aside from the stabilizing additive CeO_2 , aluminum oxide also enters into the composition of the composite ceramic studied here. Aluminum oxide is used because of the high mechanical strength and hardness of the ceramic prepared from pure aluminum oxide, but it is characterized by low fracture toughness while zirconium ceramic has high mechanical strength and low hardness. The development of a ceramic composite in the system $\text{ZrO}_2\text{--Al}_2\text{O}_3$ makes it possible to obtain simultaneously an entire complex of high mechanical characteristics, something that is unattainable in individual components of the composite.

SAMPLE PREPARATION AND STUDY METHODS

The methods for synthesizing nanoparticles in a liquid dispersion medium which are used in the present work and are based on mixing solutions of the initial, highly soluble

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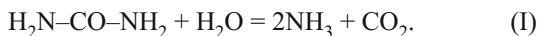
salts with the main agents (alkali, ammonia), resulting in the formation of low-solubility compounds, are used widely and successfully to obtain materials based on zirconium, cerium and aluminum oxides.

These methods are based on hydrolytic condensation of ions, which yields polynuclear hydroxo complexes, whose subsequent nucleation leads to the formation of particles with an imperfect structure (amorphous). Few results are gained from the solubility of hydroxo compounds of zirconium and cerium, and as a result they precipitate at considerable supersaturation of the solution by an autocatalytic mechanism, which impedes controlled variation of particle morphology. Subsequent aging leads to the formation of sol, gel or precipitate. The direction of the process and the properties and aggregation stability of the colloidal system depend on the initial conditions of synthesis (concentration and mixing conditions for the initial components, pH, presence of impurities, nature of the reaction products, temperature), which are difficult to reproduce. Chemical reactions, hydrolysis, olation–oxolation, complexation and polycondensation (condensation polymerization) continue to proceed against the background of coagulation processes, so that the properties of the precipitated phase depend strongly on the aging time of the system.

An alternative method of rapid precipitation using ammonia is to use compounds capable of slowly hydrolyzing and not leading to the appearance of local concentration gradients. This makes it possible to control the degree of supersaturation of the solutions and to obtain smaller, less aggregated particles.

In the present work three different basic reagents were used to synthesize Ce_{0.1}Al_{0.1}Zr_{0.8}O₂ powders: urea (sample I), hexamethylenetetramine (HMTA, sample II) and an aqueous solution of ammonia (sample III).

I. Synthesis in the presence of urea. The initial reagents were solutions of the salts ZrO(NO₃)₂ · 4H₂O (Merck 99.5%) and Al(NO₃) · 9H₂O (Merck 99.5%) + (NH₄)₂Ce(NO₃)₆ · 4H₂O (Merck 99.5%). Homogeneous hydrolysis was conducted in the presence of excess (to 1 : 5) urea at 120°C in 8 h. Urea is weakly basic and on heating in water hydrolyzes with ammonia and carbon dioxide being formed:



II. Synthesis in the presence of hexamethylenetetramine. Hexamethylenetetramine is a non-ionogenic cyclic amine easily soluble in water and capable of playing the role of a tetradeятate complexing agent. The initial solvents were prepared using ZrO(NO₃)₂ · 4H₂O (Merck 99.5%), Al(NO₃) · 9H₂O (Merck 99.5%) + (NH₄)₂Ce(NO₃)₆ · 4H₂O (Merck 99.5%), Ce(NO₃)₃ · 6H₂O (chemically pure) and hexamethylenetetramine (chemically pure). The concentration of the initial salt solutions was 0.1 M; the concentration of the HMTA solutions was 0.3 M. The solutions obtained were mixed in molar ratio 1 : 3 and kept for 1 day at room temperature, after which they were thermostated at 70°C for

3 h. When the solution is heated hydrolysis proceeds according to the equation



III. Synthesis using an aqueous solution of ammonia as the basic reagent. Solutions of the salts ZrO(NO₃)₂ · 4H₂O (Merck 99.5%) and Al(NO₃) · 9H₂O (Merck 99.5%) + (NH₄)₂Ce(NO₃)₆ · 4H₂O (Merck 99.5%) were used as the initial reagents. Precipitation was conducted by adding simultaneously drops of a solution of salts and a concentrated solution of ammonia to the initial volume 0.5 liters of distilled water with continual mixing. Solutions of salts and precipitant with concentration 0.1 M were used; the reagent feed rate was adjusted so that pH ~ 9.5 throughout the entire precipitation process.

In all three synthesis methods precipitation is controlled by hydroxide ions forming in the interaction of ammonia with water, but in the cases I and II the precipitant is released slowly and gradually. In addition, urea and HMTA can act as shape-forming substances because they can form complexes and have three-dimensional structure.

For all three methods used the products of synthesis were processed under the following identical conditions: repeated washing with water and alcohol, subsequent drying in air at 50°C in 48 h and final calcinations in air at 500°C in 3.5 h.

Cold isostatic pressing under pressure 300 MPa (press EPSI 400-200*1000Y) was used to compact the Ce_{0.1}Al_{0.1}Zr_{0.8}O₂ powder synthesized. This method yields denser, more uniform molded articles compared with uniaxial pressing, extrusion or slip casting [10].

The specific surface area of the synthesized powders was determined by the BET method according to low-temperature adsorption of nitrogen (TriStar II 3020 Surface Area and Porosity System).

The phase composition of the initial powders and ceramic composite materials was checked by x-ray phase analysis performed with a Rigaku Ultima IV diffractometer (CuK_α radiation, Ni filter).

A JEM-2100 transmission electron microscope (TEM) was used to study the size and structure of the Ce_{0.1}Al_{0.1}Zr_{0.8}O₂ powder particles.

Dilatometry (NEDTTZSCH DIL 402 C High-Temperature Dilatometer) was used to study the sintering of the ceramic. This method makes it possible to determine the basic parameters of sintering (onset and completion temperatures, shrinkage, and so on).

Atomic force microscopy (AFM) with the NTegra Aura Scanning Probe Laboratory was used to determine the topographic and structural characteristics of the ceramic obtained.

The elemental composition of the ceramic composites based on Ce_{0.1}Al_{0.1}Zr_{0.8}O₂ powder was determined by analyzing the characteristic x-ray radiation spectra which are generated by the electron beam in a scanning electron microscope (Quantum 200 3D).

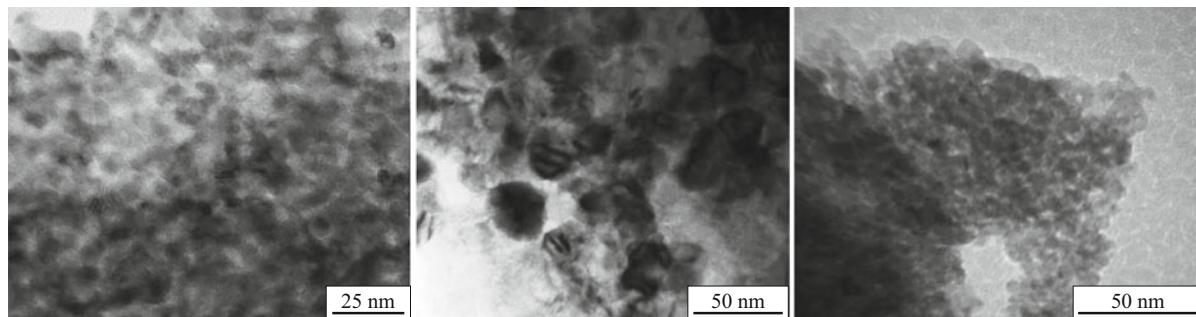


Fig. 1. SEM image of the particles of the $\text{Ce}_{0.1}\text{Al}_{0.1}\text{Zr}_{0.8}\text{O}_2$ nanopowder samples obtained by different methods. Left to right: samples I, II and III.

The density of the ceramic materials was found by the pycnometric method (Accu Pyc II 1340 Pycnometer).

The microhardness of the ceramic samples was measured by the Vickers method (DM-8 Microhardness Tester).

The cracking resistance of ceramic samples was determined by the method proposed in [11], using the expression

$$K_{1c} = 0.016 \left(\frac{E}{H} \right)^{\frac{1}{2}} \frac{F}{c^{3/2}}, \quad (1)$$

where E is Young's modulus, GPa; H is the Vickers microhardness, GPa; F is the load on the indentor, N; and, c is the crack length, m.

A NETZSCH DMA 242 Dynamic Mechanical Analyzer was used to determine Young's modulus.

EXPERIMENTAL RESULTS

Using a transmission electron microscope it was established that the particles of $\text{Ce}_{0.1}\text{Al}_{0.1}\text{Zr}_{0.8}\text{O}_2$ powder synthesized by all methods (I, II and III) are spherical with average diameter of the order of or less than 30 nm (Fig. 1), i.e., the synthesized powder is nanosize.

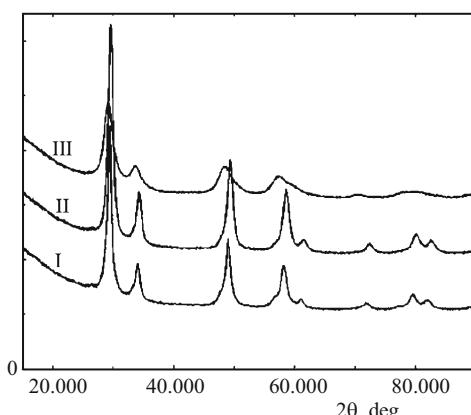


Fig. 2. Diffraction pattern of $\text{Ce}_{0.1}\text{Al}_{0.1}\text{Zr}_{0.8}\text{O}_2$ powder samples obtained by different methods: I – III) numbers of the powder samples.

The smallest powder particles (5 – 10 nm) are those obtained in the presence of urea (sample I). The particles are collected into loose formations of irregular shape with characteristics sizes 100 – 200 nm; the particle contours are indistinct. The largest powder particles (20 – 30 nm) are those obtained using HMTA (sample II). In this case the particles are rounded and less agglomerated compared with the other samples I and II. The average size of the powder particles obtained by direct precipitation of an aqueous solution of ammonia is 10 – 25 nm and these particles form quite dense formations of irregular shape with sizes to 400 nm (sample III).

The room-temperature diffraction patterns obtained from the synthesized powders are presented in Fig. 2. The lines on the diffraction patterns are somewhat broadened. This is probably due to the small size of the particles and the imperfection of the crystal structure, making it difficult to determine definitively the symmetry of the crystal lattice (cubic or tetragonal). Compared with samples I and III, sample II has the more perfect structure, since the lines in this diffraction pattern are narrower and distinct. In other words, sample II has the highest crystallinity.

The specific surface area and the particle size of the synthesized powders are presented in Table 1. The powders with the largest extended surface area are not those with the smallest average particle size but rather those with the maximum average particle size. Therefore, the specific surface area is determined not solely by the average particle size but also by other factors (specifically, the particle shape, degree of particle agglomeration and crystallinity).

The $\text{Ce}_{0.1}\text{Al}_{0.1}\text{Zr}_{0.8}\text{O}_2$ nanopowder synthesized was subsequently compacted by means of cold isostatic pressing.

TABLE 1. Characteristics of the Synthesized $\text{Ce}_{0.1}\text{Al}_{0.1}\text{Zr}_{0.8}\text{O}_2$ Powder

Powder sample	Specific surface area, m^2/g	SEM particle size, nm
I	125	5 – 10
II	165	30 – 20
III	98	15 – 25

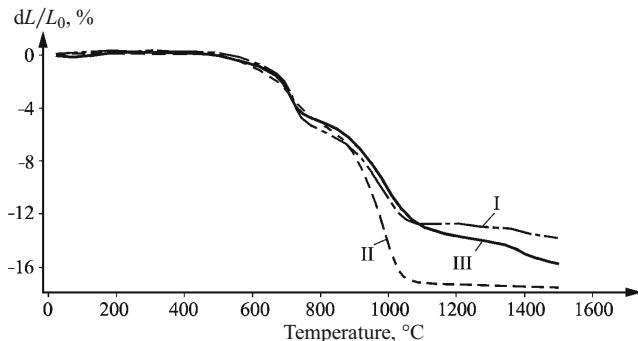


Fig. 3. Dilatometric sintering curves for pressed $\text{Ce}_{0.1}\text{Al}_{0.1}\text{Zr}_{0.8}\text{O}_2$ powder samples obtained by different methods: I – III) numbers of the powder samples.

The compacted samples were sintered in the chamber of a dilatometer in a gas atmosphere consisting of a mixture of nitrogen (80 wt.%) and oxygen (20 wt.%) with dilatometric analysis performed at the same time. The sintering temperature was 1500°C and the sintering time 2 h.

It was established that irrespective of the method used to synthesize the powder the shrinkage of all compacted samples already starts at temperature near 500°C (Fig. 3). The dilatometric curve reaches a plateau at temperature ~1050°C for sample II and about 1100°C for sample I while sample III does not sinter completely to 1500°C. The maximum shrinkage about 17% is observed for sample II. The low sintering temperatures and high shrinkage rates compared with ceramics based on conventional micron powders are due to the fact that because of the small size of the particles of the $\text{Ce}_{0.1}\text{Al}_{0.1}\text{Zr}_{0.8}\text{O}_2$ powder synthesized sintering is characterized by short diffusion distances and strong driving forces.

It is evident from the curves in Fig. 3 that sintering is a quite complex process comprising several stages. Specifically, for all samples an inflection is observed on the dilatometric curve at temperature about 700°C. The complicated shrinkage behavior of the samples on sintering could be due to polymorphic transformations occurring in the components of the composite ceramic (in aluminum oxide and zirconium dioxide) as well as several mechanisms in the sintering process (recrystallization, pore healing, and so forth).

TABLE 2. Properties of Composite Ceramic Materials Based on $\text{Ce}_{0.1}\text{Al}_{0.1}\text{Zr}_{0.8}\text{O}_2$ Powder as Functions of the Method of Synthesis of the Initial Powder

Powder sample	H , GPa	K_{lc} , MPa · m ^{1/2}	ρ_e , g/cm ³	P, %
I	1.16 ± 0.2	2.7 ± 0.3	4.79	3.2
II	2.58 ± 0.14	2 ± 0.5	4.86	2.4
III	1.28 ± 0.12	2.4 ± 0.4	4.42	4.2

The study of the post-sintering phase composition of $\text{Ce}_{0.1}\text{Al}_{0.1}\text{Zr}_{0.8}\text{O}_2$ ceramic samples established that the samples consist of two phases: the main tetragonal phase with space symmetry group $P42/nmc$, characteristic for zirconium dioxide, and an additional trigonal phase with space group $R\bar{3}c$, characteristic for corundum Al_2O_3 . It should be noted that the presence of two different phases in the experimental ceramic materials is characteristic precisely for a composite ceramic.

In addition, analysis of the Zr and Al distributions over the surface of the samples gives additional indirect confirmation that two individual phases are formed in the experimental ceramic samples. The studies showed that aluminum and zirconium accumulation zones are present in ceramic material obtained on the basis of sample I, i.e., the sample is strongly nonuniform, which is in agreement with XPA.

Microstructural analysis performed with an atomic force microscope revealed a complicated hierarchy of the microstructure of composite ceramic materials obtained from nanopowders synthesized by different methods (Fig. 4). It is evident that in all three materials studied the microstructure is comprised of chaotically oriented, rod-shaped elements, consisting of linear chains of grains of irregular shape, in the interior volume of the material. The largest grain size about 600 nm is characteristic for composite ceramic obtained from powder synthesized by precipitation of an aqueous solution of ammonia. The grain size of ceramic made from powder obtained in the presence of urea is about 350 nm. The sample based on powder synthesized under the conditions of slow hydrolysis of HMTA has the smallest grain size about 165 nm, though the average particle size of the initial powder is greatest in this case (sample II, Table 1).

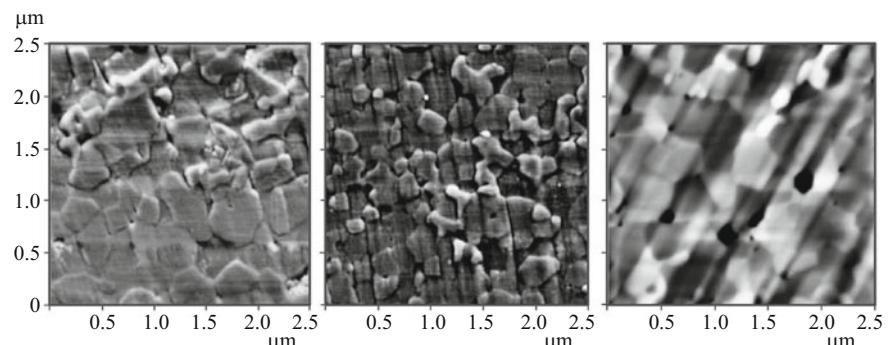


Fig. 4. AFM image of the surface of $\text{Ce}_{0.1}\text{Al}_{0.1}\text{Zr}_{0.8}\text{O}_2$ composite ceramic obtained using different initial powders: samples I, II, and III, left to right.

Mechanical tests to determine the microhardness H and cracking resistance K_{lc} were performed on the sintered ceramic samples. The values obtained as well as the density ρ_e and porosity P as functions of the type of initial powder used are presented in Table 2.

The porosity of the samples was calculated from the relation

$$P = \left(1 - \frac{\rho_c}{\rho_e} \right) \times 100\%, \quad (2)$$

where ρ_e is the experimentally determined density (pycno-metric density) and ρ_c is the density computed from measurements of the mass and geometric volume of the samples.

It is evident from the data in Table 2 that the ceramic material synthesized using HMTA (sample II) possesses the highest density (correspondingly, the lowest porosity) and the highest microhardness (lowest crack resistance in accordance with the expression (1)).

It should be noted that the values of H and K_{lc} obtained in the present work are substantially lower than the values potentially attainable in zirconium dioxide based ceramic materials [12]. This could be due to the quite low density of the samples obtained and the technology used to prepare them, which does not optimize the mechanical characteristics.

CONCLUSIONS

The following conclusions can be drawn from a comparative analysis of the results of this investigation of $\text{Ce}_{0.1}\text{Al}_{0.1}\text{Zr}_{0.8}\text{O}_2$ powder prepared by three different methods (synthesis in the presence of urea, synthesis in the presence of hexamethylenetetramine, synthesis using an aqueous solution of ammonia as the main agent) and composite ceramic materials prepared using the synthesized powder.

– Powder synthesized in the presence of hexamethylene-tetramine, in spite of the large particle size compared with the other methods of synthesis, has the highest crystallinity and largest specific surface area and lowest agglomeration.

– With compaction and subsequent sintering it is the powder synthesized in the presence of hexamethylene-tetramine that makes it possible to optimize sintering (greatest shrinkage and lowest sintering completion temperature). This could be due to better filling of the press mold with the weakly agglomerated powder with an extended specific surface area, consisting of well-formed particles with high crystallinity, which results in high density of the compacted material immediately after pressing and, therefore, provides effective conditions for sintering composite ceramic material based on $\text{Ce}_{0.1}\text{Al}_{0.1}\text{Zr}_{0.8}\text{O}_2$ powder.

– Sintering of composite ceramic material from nano-powder synthesized in the presence of hexamethylene-

tetramine makes it possible to obtain sintered material with the smallest grain size and lowest porosity and, correspondingly, maximum microhardness.

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